Effect of Solvent on Azo-Hydrazone Tautomerism of 2-Hydroxy-5-(4-nitrophenylazo)benzaldehyde

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CERTIFICATE

This is to certify that the dissertation entitled "**Effect of Solvent on Azo-Hydrazone Tautomerism of 2-Hydroxy-5-(4-nitrophenylazo)benzaldehyde"** being submitted by **Ranjita Patel** to the Department Of Chemistry, National Institute Of Technology, Rourkela-769008, for the award of the degree of Master Of Science in Chemistry, is a record of bonafide research carried out by her under my supervision and guidance. The dissertation report has reached the standard fulfilling the requirements of the regulations relating to the nature of the degree.

I further certify that to the best of my knowledge Miss. Ranjita bears a good moral character.

NIT-Rourkela

Date: **(Sabita Patel)**

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Ranjita Patel *Soubhagyabati Sahoo*

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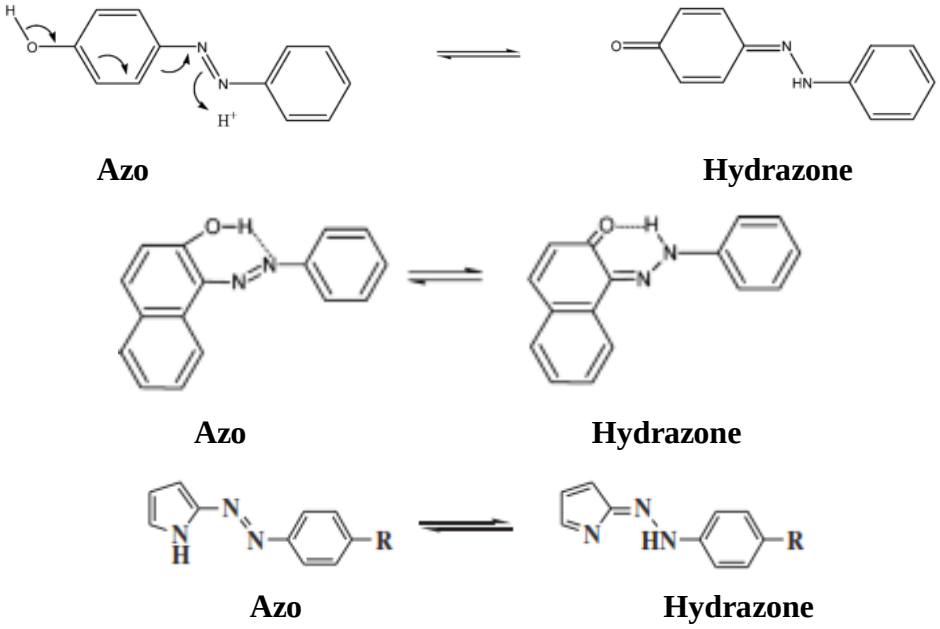
Effect of Solvent on Azo-Hydrazone Tautomerism of 2-Hydroxy-5-(4-nitrophenylazo)benzaldehyde

1. Introduction

Dyes are an important class of organic molecules which are an integral part of our lives and are used in numerous industries. For example, textile, paint and plastic industry, dye sensitized solar cells, optics, metal extraction, sensors, etc. are industriesthat depend heavily on dyes. Azo compounds are the most widely used dyes in various fieldssuch as dyeing of textiles, non-linear optics, photoswitches, chemosensors and optical data storage [1-6]. These are very important due to their brilliant color, excellent light, washing and sublimation fastness and chromophoric strength, which are the cause of their wide application as high level-dying agents in the dyestuff industry. The increasing usage of these dyes in electronic industry, such as colorimetric sensors, nonlinear optical (NLO) devices and liquid crystalline displays (LCDs) has attracted much attention [7–16]. Furthermore, some heterocyclic azo compounds have also found use as ligands to generate a special category of metal azo complexes which are exploited enormously in the manufacture of colorimetric sensors for cations, anions and small organic molecules [17-22]. In this regard, a number of studies have been devoted to the synthesis, characterization, purification and application of natural and synthetic dyes and azo dyes.

The chromophore structure of azo dyes contains two aryl rings connected through an azo bridge, Ar-N=N-Ar. The chemical and physical characteristics of the dye, like solubility or color, show variance due to the presence of different groups assubstituents on the rings. The azo dyes with a proton donor group such as –OH or -NH in conjugation (ortho- or para-) with an azo chromophore exhibit azo-hydrazone tautomerism through the transfer of proton from the donor (OH or NH) to the acceptor azo group (Scheme 1) [23]. The investigation of proton transfer between oxygen and nitrogen atoms is quite interesting from the theoretical and practical point of view. The position of tautomeric equilibrium affects the basic properties of azodyes such as colour, tone, photostability as well as technical properties of different tautomers. As a result of the intramolecular proton transfer tautomer possesses considerable differences in structure and electronic configuration from its corresponding normal species. Usually a large Stokes shift (S1 $\rightarrow$S0 fluorescence) is observed in such cases and thus used in many important applications. Some typical examples are probes for solvation dynamics and

biological environments, the development of laser dyes, ultraviolet stabilizers, metal ion sensors and scintillator counters.



Scheme 1: Azo-Hydrozone tautomers of 4-phenylazo-1-phenol (A), 2-pheylazo-1-naphthol (B) and azopyrrole (C) respectively [23-25].

1.1. Methods to analyze azo-hydrazone tautomerism

There are several experimental techniques which have been employed to study keto–enol tautomerism in azo dyes. The underlying principle is to monitor the exchange of a proton between two or more forms when the solute molecule undergoes such change. Different spectroscopic methods such as UV-Vis, FTIR, NMR spectroscopy, Mass spectrometry and single crystal X-ray analyses are commonly used methods for studying tautomerism [23].

1.2. Factors affecting tautomerism in azo dyes

Tautomerism in azo dyes is not controlled by one factor but in fact is dependent on many factors at the same time. The factors which play a major role in tuning the tautomeric equilibrium between the enol and keto forms in azo dyes in particular are

- Structure of the dye molecule
- Presence of inter- and intramolecular hydrogen bonding

- Nature of the substituent Nature of the medium surrounding the molecule such as solvent polarity, solvent type, pH of the medium, solvent-solvent and solute-solvent interactions
- Nanocaged effects
- Crystallization
- Conjugation and changes in the aromaticity
- Temperature etc.

Based on the literature review [23 and references therein] the following conclusions can be drawn.

- The presence of a strong intramolecular H-bond in the ortho derivatives e.g. 2-pheylazo-1-naphthol (Scheme 1B) has the effect of favouring the hydrazone tautomer As no such stabilization is possible in the case of the para derivatives. e.g. 4-phenylazo-1-phenol (Scheme 1A) which tends to render the equilibrium of these compounds much more susceptible to the influence of environmental factors.
- Intramolecular hydrogen bonding involving the hydrazone protons stabilize the keto form. However, the enol form is stabilized through forming an intermolecular hydrogen bonding between two units. Factors that enforce or destroy such intramolecular hydrogen bonding are pH of the media, solvent polarity, temperature, substituents, and concentration of the azo dyes. For example, changing the solvent polarity causes the change in hydrogen bonding leading to change in tautomerism.
- The electron donating and electron withdrawing properties of various substituents can stabilize a particular tautomeric form of a dye molecule either through inductive or resonance effect. Substituting an electron donating group in an azo dye favors the enol form while electron withdrawing group shifts the equillibrium towards the keto form.
- Azo dyes in the solid state have restricted motion and the major forces affecting the tautomeric form is a mostly vander Waals' force due to large p–p stacking interactions.
- Solvent can play an important role in the relative stability of the tautomeric forms. For example polar solvents promote intermolecular type of bonding between solvent and dye and thus favors the keto form, whereas nonpolar solvents favors enol form.
- Keto–enol tautomerization are known to be temperature dependent. At high temperatures, the keto form is mostly favored.

- Acidic–basic nature of the dye solution will have a profound effect on the tautomeric form of the dye. At high pH values, the labile protons usually associated with hydrogen bonding are removed thus favoring the enolate form, whereas in neutral solution the keto form is favored.

2. Objectives

Owing to the importance of azo dyes and with the advancement of knowledge, new azo dyes showing specific properties are being designed for specific uses. The physical properties of azo dyes (e.g., tone, color) are closely related with the tautomerism of the dyes. The tautomeric equilibration is generally found to depend upon their substituents as well as on the medium. The predominance of one tautomer over another is a function of many factors such as solvent polarity, solvent type, solute-solvent interactions and the structure of the dye molecule itself. With these viewpoints our objective is to synthesize an azo dye having Donor-π-Acceptor (D-π-A) system and to study the effect of solvent on the azo-hydrazone tautomerism and the relative stabilities of azo and hydrazone isomer in neat organic solvents of varied polarity and in different binary solvent mixture by means of UV-Vis spectroscopic technique.

3. Materials and Methods

The p-nitroaniline was purified by crystallizing from hot water, resulted shining light-yellow crystals. The chemicals for synthesis such as Sodium nitrate($NaNO_2$), HCl, KI are obtained from E Merck/ SISCO Chem. Salicylaldehyde was purchased from Sd-fine, India and used without further purification. Solvents were dried and purified by distillation before use as follows: Dichloromethane (CH_2Cl_2), Chloroform ($CHCl_3$), Acetonitrile (CH_3CN), Ethylacetate (EtOAc), n-Hexane from phosphorouspentoxide ($P_2O_{5)}$; dimethylsulfoxide (DMSO) and dimethyl formamide (DMF) from calcium hydride ($CaH_{2)}$; Tetrahydrofuran (THF), benzene, toluene from sodium benzophenone ketyl, n-propanol, n-butanol, isopropanol, methanol, ethanol form sodium hydroxide. Mixed solvents were prepared by carefully mixing the components by volume. Spectral measurements were taken in a double beam Shimadzu UV-Vis Spectrophotometer (UV-1800) connected with a thermostat within a temperature fluctuation of 0.1 K. All the band maxima in a particular solvent mixture were measured in a number of replicate measurements. The precision of the replicate

measurements was ±0.5 nm. Concentrations of the solute in the solutions was maintained at $3x10^{-5}$M. The energy of maximum absorption (E) was calculated from the wavelength maximum (λ_{max}) according to the following formula.

$$E\ (kcal/mol) = 28590/\lambda\ (nm)$$

3.1 Synthesis of 2-hydroxy 5-(4-nitrophenylazo)benzaldehyde

2 gm (1.44 mol) of p-nitroaniline was dissolved in a warm mixture of 5 ml concentrated HCL and 5 ml water contained in a 250 ml beaker and was placed in an ice salt bath and cooled to $0\text{-}5^0$C and stirred vigorously. A cold solution of 2 gm (4.83 mol) of sodium nitrite in 6 ml of water was added slowly with stirring to an end point with potassium iodide starch paper. 2gm(1.36 mol) of salicylaldehyde in a solution of 3.5 gm of sodium hydroxide in 12 ml water was dissolved and was cooled and added the diazotized solution slowly with stirring. Then concentrated HCL was added slowly with vigorous stirring to the cold mixture until it is strongly acid to Congo red paper. The coloured was changed from violet-dark red brown and then filtered with gentle suction, washed with water until free from acid and dried upon filter-paper in the air. The solvent was evaporated and the reaction mixture was subjected to column chromatography. Then the crude material was subjected to column chromatography. The column chromatographic separation was done in a classical glass column using silica gel (100-200 Mesh) as adsorbent and hexane:ethylacetate (8:2) mixture as eluent. The brown red coloured solid product thus obtained (4.6 gm, yield 40%, M. Pt = 127°C) was characterized from ^{1}H NMR spectral analysis. ^{1}HNMR spectrum was recorded in a Bruker 400 MHz NMR spectrometer. ^{1}H NMR (400 MHz, DMSO-d6): δ/ppm 11.485 (1H, S), 10.067(1H, S), 8.412, 8.390 (2H, d), 8.3- 8.296 (1H, d), 8.24,8.23,8.22,8.21 (1H, dd), 8.04,8.02 (2H, d), (Figure: 4). NMR analysis of the product confirmed the formation of 2-hydroxy 5-(4-nitrophenylazo)benzaldehyde.

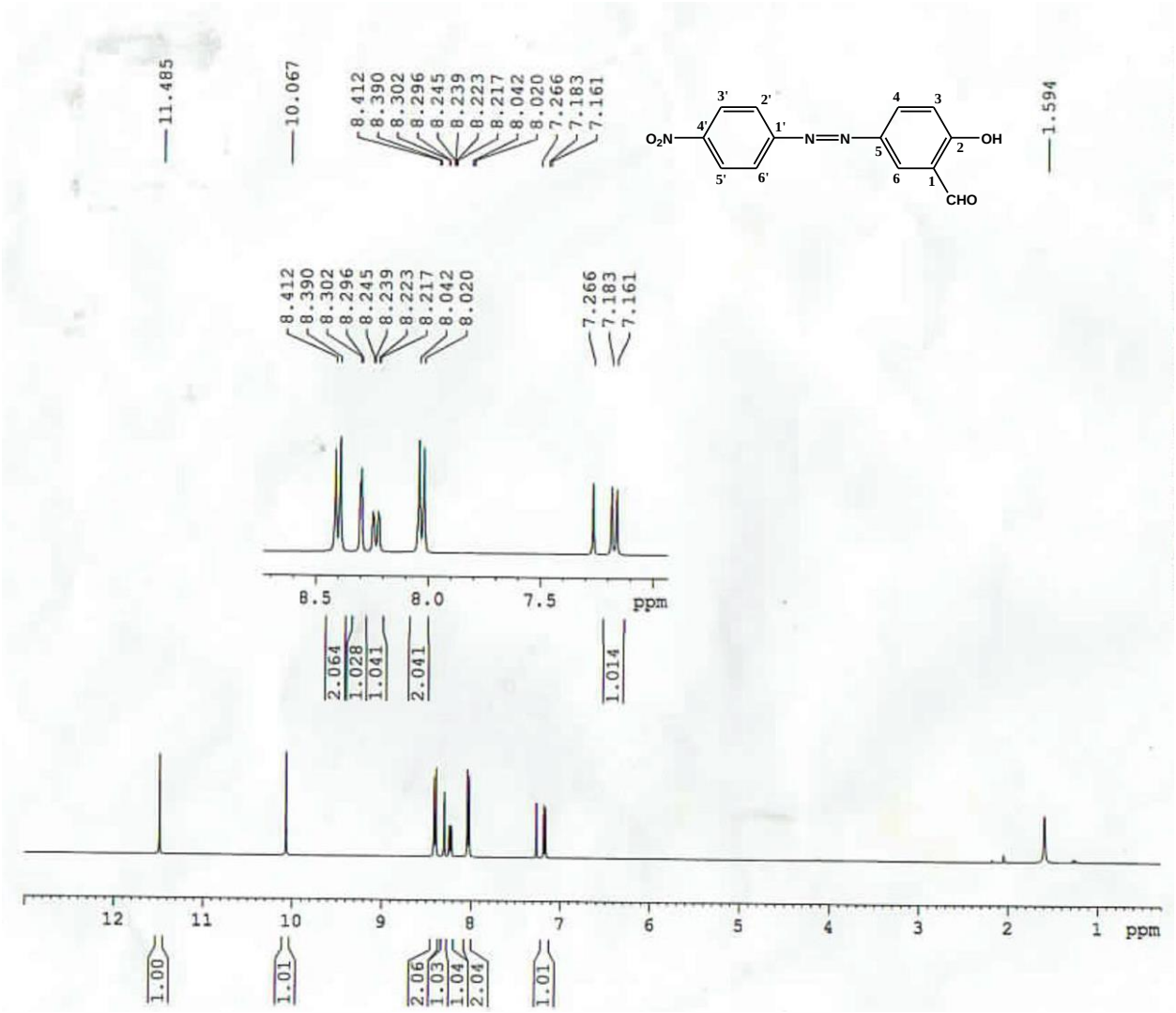
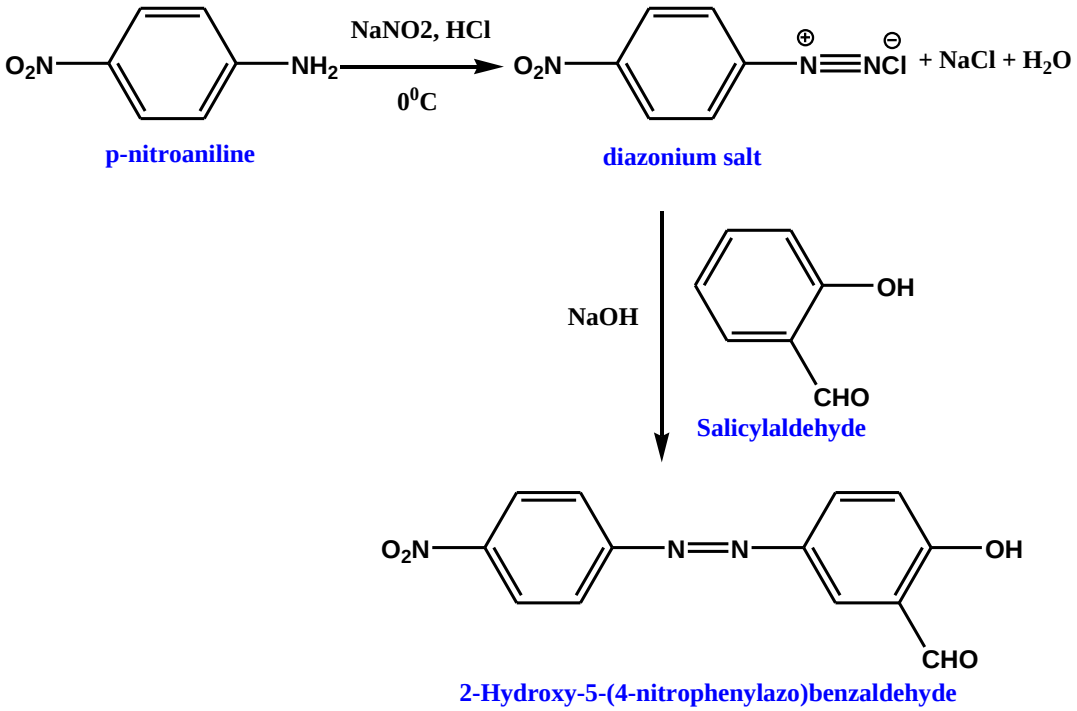


Figure 4: ^{1}H NMR spectrum of the dye 2-hydroxy 5-(4-nitrophenylazo)benzaldehyde.

4. Results and Discussions

2-Hydroxy-5-(4-nitrophenylazo)benzaldehyde is prepared by the diazonium coupling reaction of 4-nitro substituted benzene diazonium salt with salicylaldehyde in presence of sodium hydroxide (scheme 6). The synthesiszed dye is purified by column chromatographic method using hexane:ethylacetate (8:2) mixture as eluent. The brown red coloured solid product thus obtained is characterized from ^{1}H NMR spectral analysis.



Scheme 6: Synthesis of 2-Hydroxy-5-(4-nitrophenylazo)benzaldehyde

Due to the presence of exchangeable proton para to the azo functional group, it may have two tautomeric isomers (scheme 7). The UV-Vis absorption spectra of the dye were acquired in different solvent medium keeping the concentration of the dye at 3 x 10^{-5} M. To observe the solvent effect on the relative stabilities of the azo and hydrazone tautomer the UV-Vis absorption spectra were recorded in 15 different solvents differing greatly in their polarity as well as specific hydrogen bonding properties. We have divided these solvents into three different categories as follows.

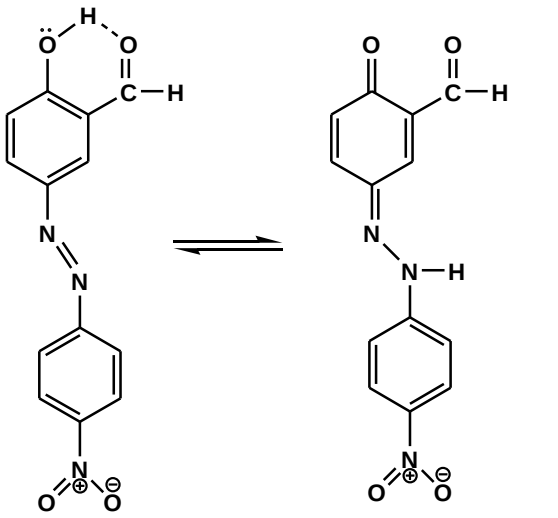
(i) nonpolar solvents (Hexane, benzene, toluene, dichloromethane, chloroform)

(ii) Dipolar aprotic solvents (ethylacetate, DMF, THF, acetonitrile, DMSO)

(iii) Polar protic solvents (Methanol, ethanol, 1-propanol, 1-Butanol and 2-propanol)

The maximum spectroscopic transition energy (λ_{max}) of the the dye originates due to $\pi \rightarrow \pi^*$ transition. Though $\pi \rightarrow \pi^*$ transition generally shows small solvatochromic shift, due the presence of donor (-OH group) and acceptor (nitrobenzene group) moieties, the ground and excited state dipole moment increases showing a large solvatochromic shift. With increase in solvent polarity, the maximum spectroscopic absorption of the dye experience a red shift (bathochromic shift) indicating a positive solvatochromism. These facts can be explained in terms of the greater stabilization of the excited state compared to the ground

state by greater solvating power of polar solvents through specific (hydrogen bonding) and nonspecific (dipole-dipole) interaction, which reduces the energy difference between ground and excited state intern reducing the maximum energy of absorption.



Scheme 7: Different tautomers of the dye 2-Hydroxy-5-(4-nitrophenylazo)benzaldehyde

In the five nonpolar group of solvents, the absorption spectrum of the dye shows a intense band around 347-358 nm ascribable to the azo form (1) along with a very low intense (virtually negligible) broad shoulder around 450 nm due to the hydrazone form (2) (Figure 5). This clearly indicates the existence of azo form predominantly. Similar characteristics in the absorption spectrum were also observed in dipolar aprotic group of solvents except DMF and DMSO (Figure 6). In the alcoholic solvents though increase in the optical density of the hydrazone band is observed the azo form was found to be present predominantly (Figure 7). All these observations clearly support the existence of predominant azo form in all the studied solvents except DMF. This fact may be attributed to the presence of intramolecular hydrogen bonding between –OH and –CHO group of the salicylaldehyde moiety which is sufficient to overcome the electron withdrawing effect of nitro group and effect of polar protic solvent towards the azo-hydrazone tautomerism and thus shifts the equilibrium towards the predominant azo form (Scheme 7). Similar effect of hydrogen bonding towards the stabilization of the azo tautomer was also observed by for the following azoquinoline derivative (Scheme 8) [30].

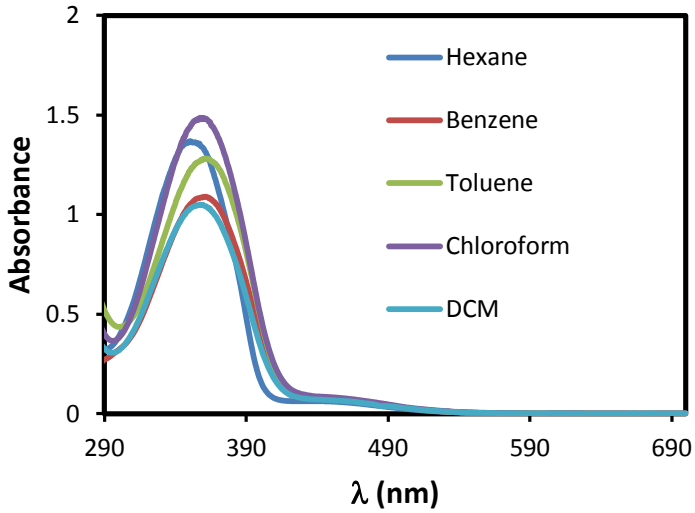


Figure 5: UV-Vis spectra of 3x10^{-5}M solution of 2-Hydroxy-5-(4-nitrophenylazo)-benzaldehyde in nonpolar solvents.

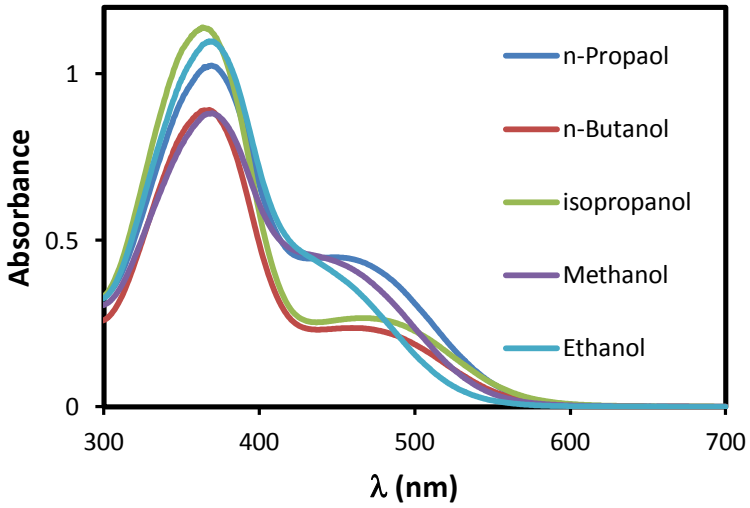


Figure 6: UV-Vis spectra of 3x10^{-5}M solution of 2-Hydroxy-5-(4-nitrophenylazo)-benzaldehyde in hydrogen bond donor solvents or polar protic solvents.

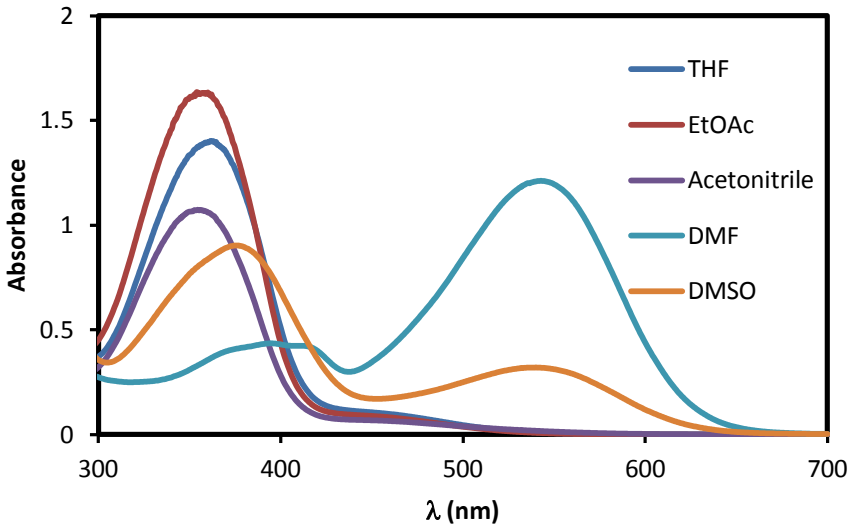
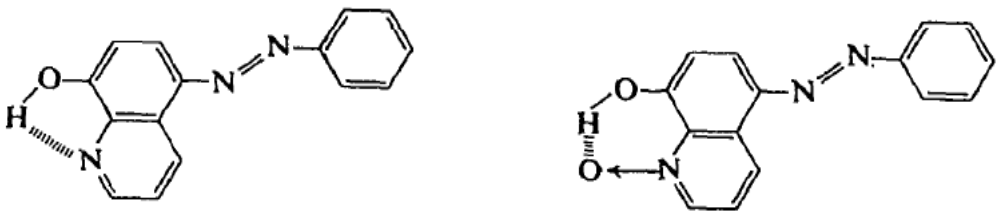


Figure 7: UV-Vis spectra of $3x10^{-5}$M solution of 2-Hydroxy-5-(4-nitrophenylazo)-benzaldehyde in polar aprotic solvents.



Scheme 8: Intramolecular H-Bonding in the azoquinoline derivative

In basic solvent like DMF, predominance of hydrazone tautomer along with large bathochromic shift of the absorption band (λmax = 540 nm) is observed. The tautomeric equilibria are influenced considerably by the ability of external hydrogen bonds between each tautomer and suitable solvents. The tautomers are stabilized to differing degrees by such bonds. The hydroxy group (-OH) in 1 is capable of stronger hydrogen bonding than the imino group (-NH-) in 2 in the proton acceptor solvents. The imino group (-NH-) in 2 is so basic that 2 is more stabilized in the proton-donor solvents such as acetic acid, chloroform and alcohols than in the proton-acceptor solvents.

The remarkably longer wavelength band in the electronic spectra in DMF and DMSO (Figure 7), may be ascribed to the anionic form due to the lengthening of the conjugated system due to the presence of electron withdrawing –NO2 group.

5. Conclusions

- We have synthesized an azo dye having Donor-π-Acceptor (D-π-A) system to study the effect of solvent on the azo-hydrazone tautomerism.
- The relative stabilities of azo and hydrazone tautomer are examined by means of UV-Vis spectroscopic technique and are correlated with the solvent properties in neat organic solvents and in different binary solvent mixture.
- Due to the presence of intramolecular H-bonding, azo form predominates in most of the nonpolar and polar protic solvents.
- Presence of low energy CT band in basic solvents like DMF is due to the predominance of anionic hydrazone form stabilized through the lengthening of the conjugated system.
- In the binary solvent mixtures, preferential solvation occurs due to specific solute-solvent interaction. The microenvironment surrounding the dye molecules played a major role in the stability of one tautomer relative to the other.
- A good understanding of the properties of specific azo dyes in different medium lead to the design of new azo dye molecules with targeted properties for applications in specific areas.

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